Final Publishable Summary for ENG09 Biofuels
Metrology for Biofuels

Background

The use of biofuels and other renewable sources for transport is promoted by Directive 2009/28/EC of the European Parliament and of the Council of April 23, 2009 ("Directive on the Promotion of the use of energy from renewable sources") whilst Directive 2009/30/EC article 7b establishes sustainability criteria for biofuels. The "White Paper on Internationally Compatible Biofuels Standards" published on 31 December 2007 by the Tripartite Task Force (BR, EU, USA) has highlighted that a series of biofuel specifications lack harmonisation between geographical regions, due to their dependence on certain methods or limit value parameters. In response to this the Task Force has recommended to "support the development of internationally-accepted reference methods and certified reference materials for improving the accuracy of measurement results that underpin the assessment of product quality, and help facilitate trade".

Need for the project

To fulfil the requirements of the EU directives, the production processes of biofuels, the characteristics of biofuel feedstocks and end products (blends), the storage, transportation, and distribution conditions must be properly monitored. However, most of the standards and measurement methods currently used for the characterisation of biofuels are drawn from specifications and test methods originally developed for fossil fuels and industrial or commercial alcohol. To assure long-term reliability and global comparability of analytical data on biofuels complete knowledge of the traceability chain is required in order to enable the establishment of traceability for measurement results of biofuel analyses to the International System of Units (SI). Traceability will also provide the legal and financial regulatory means for "trackability", determining the bio-origin of the samples/blends and their carbon dioxide contribution.

Scientific and technical objectives

This project focused on liquid biofuels used in the automotive transport industry and aimed to develop a solid measurement infrastructure able to provide reliable data and that can rapidly adapt to the changes in type and bio-origin of biofuels. The project focused on four main objectives:

- Development of references for chemical parameters
- Development of references for physical parameters
- Development of references for quality indicators
- Development of analytical tools for origin discrimination

The research activities on chemical parameters focused on improved methodologies for the characterization of chemical parameters in biodiesel such as methanol content, glycerol and glycerides content, and quantification of selected FAMEs (Fatty acid methyl esters), in order to provide a series of reference methods to ensure the accuracy and traceability of field measurements.

The legal demands for transport and trade of biofuels require very precise measurements of physical parameters such as volume and energy content (calorific value). Moreover, transport properties such as density and viscosity need accurate measurements at a broad range of temperatures and pressures, and over a long period of time to assess long-term stability, allowing the modelling of physical parameters providing equations of state. Singular measurements of different parameters already existed, but many of them were not traceable to SI and were not supported by a chemical analysis of the material. Moreover, the measurement methods were not optimised for biofuels. Reference materials were available for some

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The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

parameters at standard temperatures and pressures, but not for a sufficiently large range of temperatures. For these reasons the project dedicated part of the work to these topics.

In order to provide a faster, cheaper and more flexible assessment of the quality of biofuels, over-arching quantities (such as pH and electrolytical conductivity) are typically measured for their capability to provide a quick and simple quality assessment for biofuels for some relevant parameters such as corrosion potential and inorganic contamination. However, prior to the project serious metrological problems with respect to the comparability of measurement results existed.

Biofuels are produced all over the world, particularly in Europe, North America, Brazil and Asia. First generation biofuels are vegetable oil, biodiesel and bioethanol. They are produced from a large variety of raw materials such as rapeseed, sunflower, sugar cane, animal fat, and others. Sustainable development and use of biofuels as well as related policies on protection of the European market, climate protection and (world) food affairs require detailed information on the marketed biofuels' identity such as the country of origin, the method of production and the corresponding raw materials (organic origin). However, this is only possible if tools for verification are available.

Results

The environmental and social aspects of biofuel production are deemed very important by all experts worldwide. In the transport sector, clearly defined and internationally comparable quality standards based on traceable measurements and accurate and reliable knowledge of properties of biofuels are needed to support further technical developments which will facilitate the use of biofuels (e.g. improvement of engines and materials, development of techniques for a more efficient use of biological energy sources) and lead to greater acceptance by customers and vehicle manufacturers. Many of the methods used by field laboratories are strongly linked with regional standard methods or parameters that are method-dependent. This project, by providing reliable analytical methodology suitable for biofuels, has made important steps towards European and International harmonisation of the measurement methods of biofuels and their blends with fossil fuels.

Development of references for chemical parameters

Some of the main achievements of the project are in the development of reference methods for a selected number of important parameters that are required to be tested in biodiesel (as listed in EN 14214, "Automotive fuels – Fatty acid methyl esters (FAME) for diesel engines – Requirements and test methods" and further documentary standards referred to in this document).

The standard methods listed in EN 14214 have been developed in view of their routine use in testing laboratories, usually with the aim of developing cost efficient, fit for purpose methods. The reference methods developed within the project aimed to provide a link for the traceability of measurement data generated in biodiesel measurements and targeted four parameters: Methanol, Glycerol, Glycerides, and selected FAMEs content.

A reference method for methanol determination is now available, based on a Gas Chromatography (GC) method with an automated headspace injection system. In parallel, a Near Infrared (NIR) method has been developed as a potential on-line or at-line method. The characterisation of a glycerol calibrant was carried out providing data for the purity assessment of the calibrant. The obtained results indicated that this material was fit for purpose for use as a primary standard for the quantification of free glycerol in biodiesel. Developing glyceride measurements proved to be particularly challenging, due to the low abundance of these compounds, especially of the triacylglycerides, and to the large number of individual substances that are summarised in these sum parameters. Therefore, an approach targeting the different classes of glycerides separately with innovative measurement methods was successfully followed. Further work will be required in this complex area in future to select the best approach(es), provide the necessary calibrants and set up a traceability chain. FAMEs are the main component of a first generation biodiesel. Their quantification was addressed by developing GC-MS methods based on the use of labelled individual FAMEs for calibration.

Development of references for physical parameters

Fuels from renewable sources (biofuels) are expected to be different to fossil fuels in terms of their physical parameters. Thus, the measurement methods applied to fossil fuels, for volume measurement in particular (as this is used for the legal purpose of custody (i.e. ownership) transfer of fuels) and for process control in

the engines and industrial processes cannot be directly transferred to biofuels and fuel blends. To ensure reliable results, the physical parameters of biofuels have been determined by measurements traceable to the SI. The project addressed four measurement issues and a range of biofuels:

- Transport properties at normal pressure (density, viscosity)
- Reference materials for density and viscosity at normal pressure and temperatures (-40 to +70 °C)
- State behaviour at high temperatures and high pressures (density, viscosity)
- Energy content (calorific value)

The materials investigated were fossil diesel, rape seed methyl ester (RME) and soy bean methyl ester (SME) and the blends B5, B10, and B15. In addition RME and SME were used for the blending. For both density and viscosity, two different measurement methods were used. The comparison of the methods showed good matching of the measurement devices within their uncertainties. The energy content of the fuels was determined as calorific value in comparison to the energy of combustion under standard state conditions. Bomb combustion calorimetry in isoperibol and adiabatic mode was applied by up to three laboratories using two different commercial and one self-made calorimeter and the data was compared. Deviations between the results are covered by the repeatability and reproducibility limits given in the standards DIN 51900 and ISO 1928. Furthermore, for the first time a complete uncertainty budget for a calorimetric measurement using bomb calorimetry was estimated.

Development of references for quality indicators

The pH value of bioethanol and the biofuel's electrolytic conductivity are common measurement quantities, often used for a quick quality assessment, as a means to assess risk of corrosion and potential damage to engines. However, serious metrological problems with respect to the comparability of measurement results existed, requiring significant research effort to resolve them. The project addressed two main issues regarding the use of 'sum parameters' as 'quality indicators' for bioethanol:

- Improving the comparability of pH measurements of ethanol
- Improving the comparability of electrolytical conductivity measurements

The project developed traceability frameworks and generated reference data for these parameters.

A reference method for the measurement of ethanol/water mixtures using the Harned cell (i.e. the primary system for aqueous pH measurements) was developed. A comparison on ethanol pH measurement of a phosphate buffer in a water-ethanol mixture (50% by weight) using the Harned cell system has been performed between two project partners and two collaborators showed promising comparability between the NMIs, at a level similar to the agreement observed with aqueous buffer measurements. A reference measurement procedure to measure the conductivity of ethanol traceable to the SI, which in particular includes a reliable method to derive the solution resistance from measured impedance spectra, has been developed, based on the use of primary cell systems. Using this procedure the conductivities of a synthetic ethanol sample and bioethanol samples from different origins were measured and that were, for the first time, traceable to SI. Additionally, a detailed uncertainty calculation to assess the significance of the measurement results was developed.

Development of analytical tools for origin discrimination

Sustainable development and use of biofuels as well as related policies on protection of the European market, climate protection and (world) food affairs require detailed information on the marketed biofuels' identity such as the country of origin, the way of production and the corresponding raw materials (organic origin). Due to the complexity of the challenge and the large variety of feedstock and end-products, the project conducted a feasibility study focused on origin determination. The project addressed five key issues:

- Selection and collection of representative samples
- Bulk $\delta^{2}H$, $\delta^{13}C$, $\delta^{18}O$ analysis
- Isotope and fingerprint analysis of inorganic elements
- Fingerprint analysis of organic traces
- Compound-specific isotope analysis of $\delta^{2}H$, $\delta^{13}C$ and $\delta^{18}O$

For the first time, isotope ratio data able to discriminate between biofuels of different origin has been provided using validated and well characterised multi-methods. In particular, (i) both $\delta^{2}H$ and $\delta^{18}O$

measurements showed great potential to differentiate between oils and biodiesel of different types of raw material and geographical origin; (ii) elemental mass fraction ratios for certain element pairs, measured in the raw materials, were found to be potential tools for discrimination between biofuels of different biological (source) origin, and (iii) the ratio of specific fatty acids (e.g. linoleic acid/oleic) may have the potential to discriminate between final products (biodiesels) coming from raw materials of different biological origin.

Actual and potential impact

Dissemination of research outputs

Dissemination of the traceability concept to field laboratories through the established metrology infrastructure is a major outcome of the project. The development of references for chemical and physical parameters will contribute to the harmonisation of measurement and documentary standards across borders, which is essential for confidence in international quality assurance, needed to facilitate global trade in biofuels.

The main objective of the project was the development of reference measurement procedures of high order i.e. at NMIs and DIs. These analytical methods are not directly applicable as standard “routine” methods and therefore not directly transferable to Standardisation Bodies. However, these methods are a fundamental tool to ensure the metrological traceability of the results of routine measurements and to enable method validation and quality assurance. Furthermore, the results obtained on physical parameters provide a strong basis for legal metrology for biofuels. A robust database for thermal conversion factors and for energy content to ensure fair trade and fair calculation of tax is still needed. Care was therefore taken during the life time of the project to keep the Standardisation Bodies regularly informed of the project activities and outcomes. Main dissemination activities have been through scientific papers, conferences, direct contact with Standardisation Bodies and Proficiency Testing providers. The availability of the reference methods established in this project will allow for the provision of traceable reference values, which can eventually be disseminated through the provision of (certified) reference materials, proficiency testing schemes and other reference measurements.

The outcomes of the project were discussed at working groups of a number of European and national Standardisation Bodies:

- LNE is member of the *Bureau National du Pétrole* P08 and P06 committees, which are the mirror committees of CEN TC19 (gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin).
- VSL presented the developed reference GC method for methanol in FAME to CEN/TC19/JWG1.
- In the United Kingdom there has been interaction with relevant BSI standardisation committees who are interested in the outcomes of the project and there have been some preliminary discussions about whether some new British Standards could be developed using work on the improvement of the method for pHe.
- The activities on references for quality indicators have been presented and have stimulated debate in CEN and ISO (in particular ISO TC28/SC7/WG4 ‘Ethanol Test Methods’) about the creation of an improved test method for pHe. Participation continues on ISO TC28/SC7/WG4 as NPL has been actively involved in drafting a new standard method under a new work item entitled “Ethanol-Determination of total acidity by potentiometric titration”.
- The measurement methods developed related to origin discriminations and the need for biofuel reference materials for quality control were discussed at the UK Energy Institute's Testing Measurement and Standards Committee.

The project has also facilitated harmonisation beyond Europe. INMETRO (the Brazilian NMI) has participated in various comparisons with the project partners involved in the development of methods for the characterisation of parameters such as density, viscosity, pH and electrolytic conductivity. INMETRO has also made valuable contributions by providing bioethanol samples used in the framework of the project. In collaboration with LNE and PTB, INMETRO will co-coordinate a pilot study for pH and electrolytic conductivity of bioethanol at BIPM-CCQM level, foreseen in 2014, in order to demonstrate the feasibility of ensuring SI traceability for these parameters. The experts welcomed the work performed within the project and it is hoped that all the outcomes will have a direct influence on the documentary standard specifications for defining the quality of biofuels and in addition how these measurement can be made in future.

This project has benefited greatly from collaboration among NMI, DIs and the academic research base, involving twelve NMIs/DIs and four academic partners from ten European Countries and the EC. Some NMIs from smaller countries were also involved in the project assisting them to develop new capabilities. Furthermore, some non-European NMIs have also collaborated on specific tasks. This project consortium brought together complementary skills from both NMIs/DIs and researcher institutes to address a broad spectrum of challenging biofuels measurements, applying different analytical techniques in different scientific areas.

The coherent and complimentary international capability developed will support the traceable assessment of biofuels quality so that accurate and low uncertainty comparisons may be made over time and between locations. The project also has allowed emerging NMIs to develop new capabilities in areas where additional redundancy amongst European NMIs is welcome because of the current low number of active laboratories in certain areas.

The project has made considerable progress towards European and International harmonisation of the measurement methods of biofuels and their blends with fossil fuels and so enabling increased use:

- In the transport sector, clearly defined and internationally comparable quality standards based on traceable measurements and a wider knowledge of properties of biofuels will support further technical developments, facilitating the use of biofuels and leading to greater acceptance from customers and vehicle manufacturers
- The development of references for chemical and physical parameters will provide confidence in international quality assurance and facilitate global trade
- Traceability chains will ensure long-term reliability and global comparability, help prevent economic subsidy fraud, and improve investor confidence
- The availability of reference methods will allow for the provision of traceable reference values, which will eventually be disseminated through the supply of reference materials, proficiency testing schemes and other reference measurements

The development and implementation of a robust metrology infrastructure, which is above dispute and legal challenge, underpins the increased use of biofuels and so makes an important contribution to meeting Europe's targets for use of renewable energy sources and reduction of greenhouse gas emission, thus fulfilling the requirements of key EU sustainability directives.

List of all publically available publications

- A novel application of Recursive Equation Method for determining thermodynamic properties of single phase fluids from density and speed-of-sound measurements
  S. Lago and P.A. Giuliano Albo
  J. Chem. Thermodynamics, In press (DOI: http://dx.doi.org/10.1016/j.jct.2012.10.016)
- Sensitivities of a Standard Test Method for the Determination of the pHe of Bioethanol and Suggestions for Improvement
  R. J. C. Brown, A. C. Keates and P. J. Brewer
  Sensors, 2010, 10, 9982 - 9993. (http://www.mdpi.com/1424-8220/10/11/9982/pdf)
- Influence of fabrication procedure on the electrochemical performance of Ag/AgCl reference electrodes
  D. Stoica, P. J. Brewer, R. J. C. Brown, P. Fisicaro
  Electrochmica Acta, 2011, 56, 10009 - 10015.
  (http://www.sciencedirect.com/science/article/pii/S0013468611013363)
- Evaluation of standard potential of Ag/AgCl electrode in a 50 wt% water-ethanol mixture
  D. Stoica, C. Yardin, S. Vaslin-Reimann, P. Fisicaro
  Journal of Solution Chemistry, 2011, 40, 1819 - 1834.
  (http://link.springer.com/article/10.1007%2Fs10953-011-9758-3)
- Electrolytic Conductivity as a Quality Indicator for Bioethanol
  S. Seitz, P. Spitzer, H.D. Jensen, F. Durbiano

Proceedings of XX IMEKO World Congress Metrology for Green Growth
(http://www.imeko.org/publications/wc-2012/IMEKO-WC-2012-TC20-O12.pdf)

- Determination of pH values of potassium hydrogen phthalate buffer in water-ethanol mixture (mass fraction 50 %)
  D. Stoica, P. Fisicaro, P. Spitzer, B. Adel, F.B. Gonzaga, I.C. Fraga, P.P Borges, I. Maksimov, T.Asakai
  Proceedings of XX IMEKO World Congress Metrology for Green Growth
  (http://www.imeko.org/publications/wc-2012/IMEKO-WC-2012-TC24-O4.;pdf)
- Fatty acid composition and chemotaxonomic evaluation of species of Stachys
  Ahmet C. Gören, Ekrem Akçicek, Tuncay Dirmenci, Turgut Kilic, Erkan Mozioğlu, Hasibe Yilmaz
  Natural Product Research, 2012, 26, 84–90
- Density, viscosity and speed of sound measurements specific heat capacity of a summer diesel with components of rapeseed or soybean methyl ester
  H. Wolf, R. Pagel , S. Lago, P. A. Giuliano Albo, P Ballereau
  Fuel, Submitted
- Experimental speed-of-sound measurements of pure fatty a ids methyl ester, mineral diesel and blends in a wide range of temperature and for pressures up to 300 Mpa
  P. A. Giuliano Albo, S. Lago
  Fuel, Submitted
- Density, viscosity and speed of sound measurements specific heat capacity of a summer diesel with components of rapeseed or soybean methyl ester
  H. Wolf, R. Pagel , S. Lago, P. A. Giuliano Albo, P Ballereau
  Fuel, Submitted

JRP start date and duration:	1st June 2010, Duration 36 months
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JRP-Partners: JRP-Partner 1 BAM, Germany JRP-Partner 2 DFM, Denmark JRP-Partner 3 INRIM, Italy JRP-Partner 4 JRC, European Commission JRP-Partner 5 LGC, United Kingdom JRP-Partner 6 Metrosert, Estonia	 JRP-Partner 7 NPL, United Kingdom JRP-Partner 8 PTB, Germany JRP-Partner 9 SP, Sweden JRP-Partner 10 TUV NEL, United Kingdom JRP-Partner 11 TUBITAK, Turkey JRP-Partner 12 VSL, The Netherlands
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The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union